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SYNTHESIS OF SPINEL CERAMIC PIGMENTS AND GLAZES BASED ON THEM

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The results of research on the synthesis of ceramic pigments based on titanomagnetite with modifying additives zinc, magnesium, cobalt and manganese oxides are presented. X-ray phase analysis is used to determine the phase compositions of the pigments as a function of the composition and synthesis temperature. The optimal compositions and synthesis conditions of pigments are determined.

Key words: titanomagnetite, metal oxides, synthesis, pigments, spinels, glazes.

Ceramic pigments can be obtained by cryochemical and plasma-chemical methods, co-precipitation, sol-gel technology and other means as well as by solid-phase synthesis at high temperatures. The latter method is widely used because it does not require specialized complicated and expensive equipment. In solid-state synthesis it is important to control not only the chemical composition but also the microstructure of the product. This is because the chemical properties (activity in solid-phase reactions) and many physical properties (optical, magnetic, electric and others) depend on the structural organization of the solid. The most important factors determining the properties of the desired products are the elemental composition of the solid, the particulars of the coordination environment of the atoms in crystalline and amorphous bodies as well as the composition and concentration of point defects [1].

The spinel lattice is one of the most suitable crystal lattices for developing a large range of stable ceramic paints. The lattice contains ions with different valence in octahedral and tetrahedral coordination. This opens up the possibility of tinting glazes in different colors by using a particular element and changing its valence state or degree of oxidation, since the color in which the ions in silicate systems are colored depends mainly on their valence state and coordination number [2].

Transition elements possessing chromophoric properties and characterized by the presence of an unfilled *d*-shell (V, Cr, Mn, Fe, Co, Ni, Cu) are the most commonly used coloring compounds; rare-earth elements characterized by an unfilled *f*-shell are less often used.

Heat-resistant ceramic pigments are obtained on the basis of the crystal structures of spinel, garnet, diopside and so forth. Natural minerals distinguished by high proclivity toward isomorphism are used to expand the palette of ceramic pigments: perovskite, talc and wollastonite. Natural minerals lower the cost of pigments [3].

Wastes and byproducts from the mining industry are usually used to obtain pigments for ceramics. For example, iron-containing wastes are used to obtain black and brown pigments [4]. Pigments are also synthesized on the basis of concentrates of ilmenite from different deposits. It has been determined that the titanium oxide present in them intensifies the chromophoric properties of iron [5]. From this standpoint titanomagnetite is very promising for use as a raw material in the synthesis of ceramic pigments.

Titanomagnetites form a large group of minerals which are solid solutions or mechanical mixtures of ilmenite and magnetite. The ratios of the oxides in the chemical composition fluctuate, mainly because titanomagnetite forms strong concretions with other minerals: aegirine, apatite and lepidomelane.

Titanomagnetite concentrate (Apatit, JSC) obtained from the processing of apatite-nepheline ore was used for the present investigations. This is a fine powder with the fraction < 0.07 mm predominating. The titanomagnetite content in the concentrate was 95%[5] with sphene, apatite, aegirine and nepheline present as impurities.

The impurities were partially removed from the titanomagnetite. The chemical composition is (%): 32 – 37 Fe_2O_3; 36.0 – 45.0 FeO; 14.5 – 16.5 TiO_2; 1.0 – 4.0 SiO_2; 1.4 –

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[5] Here and below the content by weight, wt.%.

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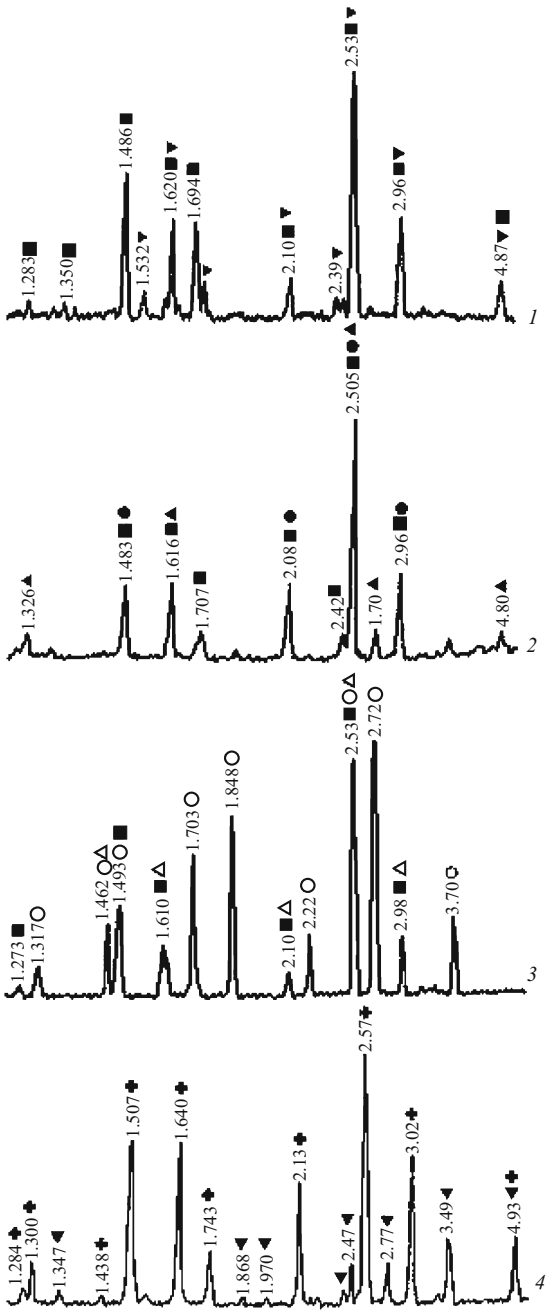


Fig. 1. X-ray diffraction patterns after firing at 1200°C: *1*) titanomagnetite 60% + zinc oxide 40%; *2*) titanomagnetite 60% + magnesium oxide 40%; *3*) titanomagnetite 60% + cobalt oxide 40%; *4*) titanomagnetite 50% + manganese oxide 50%; □) zinc ferrite $ZnFe_2O_4$; ▶) zinc titanate Zn_2TiO_4; ■) magnetite Fe_3O_4; ●) magnesium ferrite $MgFe_2O_4$; ✳) magnesium titanate $MgTiO_4$; ◁) cobalt ferrite $CoFe_2O_4$; ○) cobalt titanate $CoTiO_3$; ▼) $Fe_2MnTi_3O_{10}$; ✚) manganese ferrite $MnFe_2O_4$.

1.9 CaO; 1.6 – 2.0 MnO; 0.2 – 0.5 P_2O_5; 0.3 – 0.5 V_2O_5; 0.4 – 0.9 MgO; 0.3 – 0.9 Na_2O; and, 0.2 – 0.6 K_2O.

Modifying additives in the form of zinc and magnesium oxides as well as the chromaphore oxides MnO_3 and CoO were used to synthesize ceramic pigments based on titanomagnetite concentrate. For sample preparation the titanomagnetite concentrate was first washed with distilled water, dried at temperature 110°C, and comminuted to complete passage through a 0.05 mm sieve. The batch for synthesizing the pigments was prepared with the corresponding oxides. The oxide content in the mixtures ranged from 10 to 90%. The ready batch was loaded into corundum crucibles and fired in an electric furnace to maximum temperature from 750 to 1200°C in 50°C step. The change in the phase composition of the pigments obtained as a function of the firing temperature and composition was studied by x-ray phase analysis. To determine the coloring properties the pigments were mixed with glaze frit. The pigment content in the frit varied from 3 to 7%. Pellets were molded from the mixture and fired in a silit furnace. A 3% solution of polyvinyl alcohol was used as binder. The firing temperature was raised at the rate 180 K/h and held at the final value for 1 h. The firing interval was 1060 – 1080°C.

According to the phase composition in the system titanomagnetite – metal oxide as a function of the synthesis temperature and batch composition successive substitution of modifier ions occurs in all cases. In the process spinel type compounds are formed: ferrites and titanates of the cations introduced [6 – 8].

The reactions proceed according to the following general scheme:

$$Fe_3O_4 + FeTiO_3 + Fe_2TiO_4 + 7MeO + 2O_2 = 3MeFe_2O_4 + 2Me_2TiO_4.$$

Spinel compounds start to form at firing temperature 800 – 850°C; the process stops at 1100 – 1200°C. The highest degree of completion of synthesis obtains with isothermal soaking for at least 4 h. Phase formation stops at 1200°C in practically all systems studied. Microscopic studies have shown that as a result of synthesis up to 60% of the compounds formed have spinel structure. Spinel-type crystalline materials usable as ceramic pigments in glazes were synthesized in the systems ZnO–MgO–CoO with the components in the ratio titanomagnetite : oxide = 1.5 : 1 in the batch and firing temperature 1200°C. The optimal ratio of the components in the titanomagnetite – Mn_2O_3 system is 1 : 1. If this ratio is tilted toward higher Mn_2O_3 content, two iron ions are replaced with manganese ions in the ferrospinel structure. A spinel structure with composition $MnMn_2O_4$ is formed.

A comparison of the x-ray spectra of titanomagnetite with the spectra of mixtures with Zn, Mg, Co and Mn oxides shows that the x-ray spectra of the mixture obtained after firing are very close and rare exceptions aside do not permit definitive identification of the new compounds that appear as a result of high-temperature synthesis (Figs. 1 and 2). The phase composition of the materials obtained is presented in Table 1.

The qualitative phase compositions of the experimental systems based on titanomagnetite, as determined according

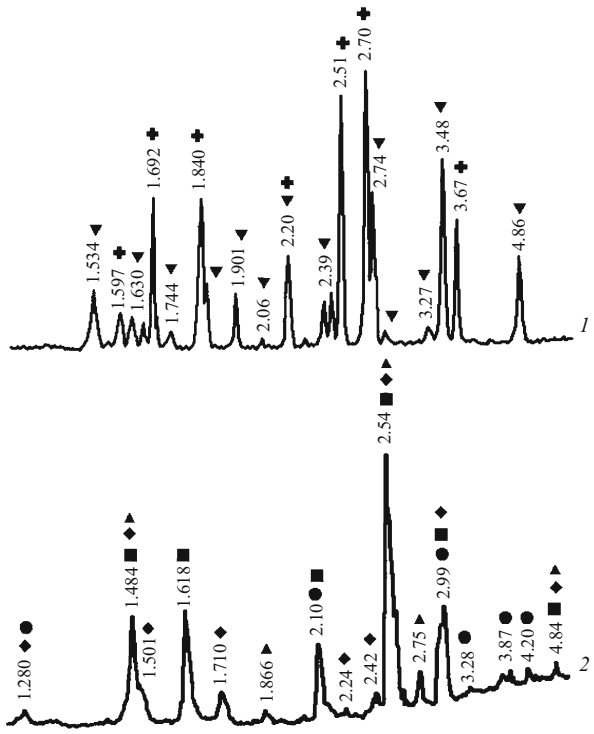


Fig. 2. X-ray diffraction pattern of titanomagnetite: *1*) green body; *2*) firing at 1200°C; ■) magnetite; ●) nepheline; ◆) ulvespinel (Fe_5TiO_8); ▲) ilmenite ($FeTiO_3$); ▼) pseudobrookite (Fe_2TiO_5); ✚) hematite (Fe_2O_3).

to the x-ray spectra using data from a quantitative chemical analysis, are presented in Table 1.

These investigations have shown that up to 40% addition of pure oxides is required to synthesize the spinel structure of the pigments obtained. For coloring and to obtain a range of colors for glazes from light to dark tones pigments are introduced into the batch in amounts from 3 to 7%. The need for pure starting oxides decreases, which lowers the cost of the glazes.

The interaction of the ceramic pigments with silicate melt during synthesis of glazes based on them produces an amorphous structure and changes the color of the initial pigment (Table 2).

In summary, the pigments obtained as a result of the synthesis of ceramic pigments based on titanomagnetite withstand high temperatures and can be used to color transparent and opacified glazes.

REFERENCES

1. P. P. Budnikov and A. M. Ginstling, *Reactions in Mixtures of Solid Substances* [in Russian], Stroiizdat, Moscow (1971).
2. I. V. Pishch and E. V. Radionov, "Synthesis of pigments based on perovskite," *Steklo Keram.*, No. 8, 23 – 24 (1998).
3. S. T. Tumanov, "Synthesis of ceramic paints," in: *Physical and Chemical Principles of Ceramics* [in Russian], Promstroiizdat, Moscow (1956), pp. 287 – 292.
4. N. A. Mikhailova, I. T. Akhmerov, and É. G. Vovkotrub, "Decorative coatings for ceramics based on industrial wastes from the Ural region," *Steklo Keram*., No. 3, 20 – 21 (1997); N. A. Mikhailov, I. T. Akhmerov, and É. G. Vovkotrub, "Decorative ceramic coatings based on industrial wastes of the Ural region," *Glass Ceram*., **54**(3 – 4), 88 – 89 (1997).
5. N. F. Shcherbina, T. V. Kochetkova, and V. E. Eliseeva, "Brown ceramic pigment, RF Patent 2248333, MPK^7 C 03 1/04, C 04 B 41/86; patent holder Institute of Chemistry and Technology of

TABLE 1. Phase Composition of Synthesized Pigments Based on Titanomagnetite (t/m) with Different Firing Temperatures

Optimal pigment composition, %*	Phase composition with firing temperature, °C			
	800	950	1000	1200
t/m : ZnO (60 : 40)	Magnetite, spinels: zinc ferrite, zinc titanate, zinc α-titanate	Spinels: zinc ferrite↑, zinc titanate↑	Spinels: zinc ferrite↑, zinc titanate↑	Spinels: zinc ferrite↑, zinc titanate↑
t/m : MgO (60 : 40)	Pseudobrookite, hematite, magnetite, magnesium oxide, spinels: magnesium ferrite	Hematite↓, magnesium oxide↓, magnesium metatitanate↓, spinels: magnesium ferrite↑, magnesium titanate	Magnetite, magnesium oxide↓, spinels: magnesium ferrite↑, magnesium titanate↑	Magnetite↓, spinels: magnesium ferrite↑, magnesium titanate↑
t/m : CoO (60 : 40)	Pseudobrookite, hematite, cobalt oxide, spinels: cobalt ferrite, cobalt titanate	Hematite↓, cobalt oxide↓, spinels: cobalt ferrite↑, cobalt titanate↑	Magnetite↓, spinels: cobalt ferrite↑, cobalt titanate↑	Magnetite↓, spinels: cobalt ferrite↑, cobalt titanate↑
t/m : Mn_2O_3 (50 : 50)	Pseudobrookite, hematite, MnO, Mn_2O_3, spinels: manganese ferrite	Hematite↓, MnO↓, Mn_2O_3, spinels: manganese fer - rite↑	Hematite↓, MnO↓, Mn_2O_3, spinels: manganese fer - rite↑	Spinels: manganese ferrite↑, $Fe_2MnTi_3O_{10}$

* Content by weight.

Notations: ↑↓) increase, decrease of the content, respectively.

TABLE 2. Color Change of Glaze as a Function of the Content and Type of Modifying Oxide

Oxide	Oxide content in batch, %	Glaze color			
		Pacified nepheline glaze	Transparent nepheline glaze	Opacified cerium glaze	Opacified zirconium glaze
ZnO	10	Light brown	Dark blue	Light gray	–
	20	Beige	Dark blue	Light gray	–
	30	Beige	Lilac	Light gray	–
	40	Beige	Lilac with gold inclusions	Light gray	–
MgO	10	Sandy	Dark lilac	Cream	Beige
	20	Sandy	Light blue	Cream	Beige
	30	Sandy	Light blue	Cream	Beige
	40	Sandy	Light gray	Cream	Beige
Mn_2O_3	10	Beige	Dark blue with brown inclusions	Light brown	Gray brown
	20	Light brown	Dark blue with brown inclusions	Light brown	Gray brown
	30	Brown	Blue	Light brown	Gray brown
	40	Brown	Blue	Light brown	Beige

Rare Elements and Minerals, Kola Scientific Center of the Russian Academy of Sciences, No. 2003119671/03," application June 30, 2003; published March 20, 2005; *Byull. Izobr. Polezn. Modeli*, No. 8 (2005).

6. N. F. Shcherbina, T. V. Kochetkova, and V. E. Eliseeva, "Glaze, RF Patent 2302387, MPK[7] C03 C8/08(2006.1); patent holder Institute of Chemistry and Technology of Rare Elements and Minerals, Kola Scientific Center of the Russian Academy of Sciences, No. 2005136625/03," application November 24, 2005; published July 10, 2007; *Byull. Izobr. Polezn. Modeli.*, No. 19 (2007).
7. N. F. Shcherbina and T. V. Kochetkova, "Investigations of the conditions of synthesis and properties of spinels based on titanomagnetite," in: *All-Union Scientific Conference with International Participation on the Scientific Principles of the Chemistry and Technology of Raw Materials Processing and Synthesis of Functional Materials Based on Them: Collection of Scientific Works, Apatity, April 8 – 11, 2008* [in Russian], Izd. KNTs RAN, Apatity (2008), Pt. 2, pp. 234 – 235.
8. N. F. Shcherbina, P. A. Kosobokova, and V. Ya. Kuznetsov, "Study of the behavior of titanomagnetite concentrate during heating," in: *Scientific Work: Chemistry, Technology and Properties of Silicate Materials* [in Russian], Izd. KNTs RAN, Apatity (1999), pp. 18 – 22.